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WADD TECHNICAL NOTE 60-269

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RESEARCHES ON HYDROGEN OVERTVOLTAGE ON METALLIC SINGLE CRYSTALS: CADMIUM

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FEBRUARY 1961

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Materials Central

Contract No. AF 61(052) - 144

Project No. 7022

**WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This report was prepared by Laboratori di Elettrochimica, Chimica fisica e Metallurgia del Politecnico di Milano, Milano, Italy, under USAF Contract No. AF 61(052)-144. This contract was initiated under Project No. 7022, "Surface & Interface Phenomena of Matter", Task No. 73660, "Cathodic Processes Which Involve Release of Hydrogen". The work was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Dr. R. J. Barton acting as project engineer.

This report covers work conducted from June 1959 through July 1960.

ABSTRACT


Hydrogen overvoltage on cadmium polycrystalline and single crystal cathodes, oriented following the (0001), (1010) and (1120) planes, has been measured in perchloric acid solutions.

The Tafel law holds nearly; the parameters being different for the different electrodes.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:


J. H. PAGANO,
Major USAF

Actg Chief, Advanced Metallurgical
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I. Introduction

Earlier work by authors on hydrogen overvoltage on cadmium electrodes in acid solutions is in disagreement relative to the results and to the values obtained among themselves.

In 1946 Pecherskaya and Stender (1) verified the validity of the Tafel law for cadmium electrodes in 2 N H_2SO_4 and in 1 N HCl, between 10 and 2000 A/m^2 , in opposition to earlier results of Hickling and Salt (2), who found that for cadmium electrodes in 1 N HCl overvoltages approach a constant value at a c. d. of about 100 A/m^2 .

Kolotyркиn and Medvedeva (3) working in a lower c. d. range (between 0,01 and 10 A/m^2) encountered in 1,3 N H_2SO_4 an upward overvoltage shift from - 0,75 V to - 0,92 V at a c. d. of about 1 A/m^2 ; while on either side of the shift the plot overvoltage vs. c. d. followed Tafel's equation with a slope of about 0,12 V.

The authors give evidence that the shift appeared for an overvoltage value corresponding to the zero charge of the surface, and that the two branches referred to differently charged surfaces.

Indeed the upper branch was independent of the nature of the anion (the position remaining practically the same in 1,3 N H_2SO_4 and in 1,15 N HCl), while, on the contrary, the lower branch, lay distinctly higher in HCl than in H_2SO_4 .

The influence of the concentration of the same acid (0,1 ; 1,7 and

Manuscript released by authors June 1960 to be published as a WADD Technical Note.

10 N H_2SO_4) was different on the two branches. At high c. d., overvoltage depended on the concentration of the acid only above 1 N, whereas at lower c. d., overvoltage depended on the concentration only below 1 N and was independent of it at higher acid concentration.

As a consequence of this behavior, Cd electrodes in 0,1 N H_2SO_4 did not present the shift.

E. Albrecht (4) determined hydrogen overvoltage on (0001) oriented Cd electrode in 1 N H_2SO_4 , between 10 and 300 A/m^2 .

Moreover he found two Tafel lines, shifted one from the other about 100 mV, while polycrystalline cadmium had about an intermediate position, but with a smaller slope (0,08 V than 0,13 V).

In table I are reported for comparison numerical values obtained from the above mentioned different authors.

The results, as stated, are not in agreement, but could be divided into two classes, according to the range of overvoltage values.

The Tafel law holds also for alkaline solutions (0,2 to 15,4 N KOH; 0,6 N NaOH and 6 N NaOH), (7, 8, 9). Also in this case, while the values of b determined by the different authors are nearly the same, the values of a vary over a wide range.

Examples are reported in table I.

Following our research program concerning hydrogen overvoltage on SCE (10), the behavior on cadmium (0001), (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) SCE and on polycrystalline cadmium has been investigated in perchloric acid baths of different concentration (from 0,005 to 0,035 M) at 25, 40 and 55°C, with c. d. up to 10 A/m^2 .

II. Experimental technique

For the experimental details and pre-electrolysis conditions, we refer to the preceeding technical-scientific note (No. 2).

Before each measurement the electrode surfaces were electro-polished in phosphoric acid bath (4,5 cm³ H_3PO_4 in 5,5 cm³ H_2O) at a

c. d. of 500 A/m^2 (applied voltage: 2 V).

The electrodes were successively treated as cathodes in a fresh solution, to develop hydrogen on the surface.

The most regular results were obtained after pre-polarizing the electrodes as cathodes in the measurement cell for 3 to 4 hours at 15 A/m^2 .

Pre-electrolysis conditions were: $50\text{--}60 \text{ Coulombs/cm}^3$ at a current intensity of 0,05 A, with a cathodic platinum surface of $0,05 \text{ cm}^2$ for each cm^3 of solution.

III. Overvoltage measurements

In our measurements steady values were reached very slowly; moreover the values obtained with decreasing c. d. are always more reproducible and sometimes a little higher than those obtained with increasing c. d.

Fig. 1 and 2 are typical examples of the curves overvoltage vs. c. d. at different temperatures.

The first one refers to $(10\bar{1}0)$ Cd in $0,020 \text{ M HClO}_4$, the second one to $(11\bar{2}0)$ Cd in $0,005 \text{ M HClO}_4$. The Tafel law is followed.

In Fig. 3 the dependence law of overvoltage values upon time, at constant c. d., is given by oscillographic recordings for (0001) Cd in $0,035 \text{ M HClO}_4$ ^{x)}.

During the initial build-up of overvoltage, $\Delta\eta$ relatively quickly reaches constant values, while the overvoltage decay is definitely slower.

In tables II to V the experimental values are reported for: Tafel constants a and b, exchange c. d. i_0 , overvoltage at two different c. d. (at $0,1$ and 10 A/m^2) and for the standard heat of activation of the hydrogen evolution reaction, ΔH .

Reproducibility being not always satisfying, results are average

^{x)} Negative overvoltage values ($\Delta\eta$) are here shown as rising curves.

values of numerous measurements (deviations not exceeding 10 % of the given values).

Behavior in perchloric acid

The overvoltage, the other parameters being constant, is influenced by the orientation.

For dilute solutions, at all of the temperatures investigated, overvoltage increases following the order: $(0001) < (11\bar{2}0) < (10\bar{1}0)$, while polycrystalline cadmium presents an intermediate behavior.

With increase in concentration, the overvoltages for (0001) and polycrystalline electrodes are increased in opposition to what is usually found (Fig. 4), while those of the other two SCE decrease.

This behavior difference is able to change the order of the overvoltage found for dilute solutions.

Indeed for concentrated solutions overvoltage increases following the order: $(11\bar{2}0) < (10\bar{1}0) < (0001)$, at all temperatures, as reported in Fig. 5.

Polycrystalline Cd has again an intermediate value.

IV. Conclusions

- 1) Temperature influence is regular, overvoltage decreasing with increasing temperature.
- 2) The influence of the acid concentration depends on the nature of the electrodes. Indeed increasing acid concentration:
 - a) for $(10\bar{1}0)$ and $(11\bar{2}0)$ Cd overvoltage decreases;
 - b) for polycrystalline Cd and, to a greater extent for (0001) Cd, overvoltage increases.
- 3) The most densely packed plane (0001) presents thus: the lowest overvoltage values in dilute solutions and the highest ones in more concentrated solutions.

- 4) The empirical law of the anticorrelation between kinetics activity as far as the metal ions exchange on the one hand and hydrogen ions exchange on the other one is concerned, is confirmed also for cadmium. This metal has rapid exchange of its ions (11) but high overvoltage values.
- This anticorrelation does not appear for the orientation influence, which is in the first case very small.
- 5) Comparing our results with those of the preceeding studies (see table I), we could observe:
- a) there is no overvoltage shift, maybe because the solutions are very dilute compared to those used by Kolotyrkin and Medvedeva (3), as found also by G. Belmondi (6) for 1 N HClO_4 solutions;
 - b) the overvoltage and b values are intermediate between those obtained by the other authors.

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TABLE I

Authors	Orientation	Solution	b (mV)	Overvoltage at	
				1 A/m ² (mV)	10 A/m ² (mV)
Pecherskaya-Stender (1)	Polycryst. Cd	2 N H ₂ SO ₄	210	-	510
Albrecht (4)	Polycryst. Cd (0001) Cd	1 N H ₂ SO ₄	76	-	550
Sergeev (5)	Polycryst. Cd	1 N H ₂ SO ₄	130	-	500-580
Hickling - Salt (2)	Polycryst. Cd	H ₂ SO ₄	-	360	570
Kolotyrkin - Medvedeva (3)	Polycryst. Cd	1 N HCl	250	-	990
Belmondi (6)	Polycryst. Cd	0, 1 N H ₂ SO ₄	120	900	1020
		1, 3 N H ₂ SO ₄	120	shift	1020
	Polycryst. Cd	1 N HCl	137	980	1115
		1 N H ₂ SO ₄	137	1245	1380
		1 N HClO ₄	144	1318	1460
This work	Polycryst. Cd	0, 02 N HClO ₄	150	635	790
Zholuder - Stender (7)	Polycryst. Cd	6 N NaOH	160	-	580
Jofa - Braun (8)	Polycryst. Cd	6 N KOH	135	-	915
Genta - Belmondi (9)	Polycryst. Cd	6 N KOH	110	1365	1475

TABLE II

Electrode: (0001) Cd

Solution	Temp. (°C)	a (mV)	b (mV)	log i_o (A/m ²)	Overvoltage at		ΔH (Kcal)
					0.1A/m ² (mV)	10A/m ² (mV)	
HClO ₄ 0,005M	25	545	135	-4,05	410	680	-
	40	525	125	-4,20	400	655	
HClO ₄ 0,020 M	25	665	130	-5,10	530	790	-
	55	640	110	-5,80	530	750	

TABLE III

Electrode: (10 $\bar{1}$ 0) Cd

Solution	Temp. (°C)	a (mV)	b (mV)	log i_o (A/m ²)	Overvoltage at		ΔH (Kcal)
					0.1A/m ² (mV)	10A/m ² (mV)	
HClO ₄ 0,005 M	25	630	140	-4,50	490	770	-
	55	605	130	-4,65	470	731	
HClO ₄ 0,020 M	25	610	100	-6,10	515	710	6
	40	590	100	-5,90	490	730	
HClO ₄ 0,035 M	25	610	115	-5,30	495	725	8
	40	570	115	-5,00	460	685	

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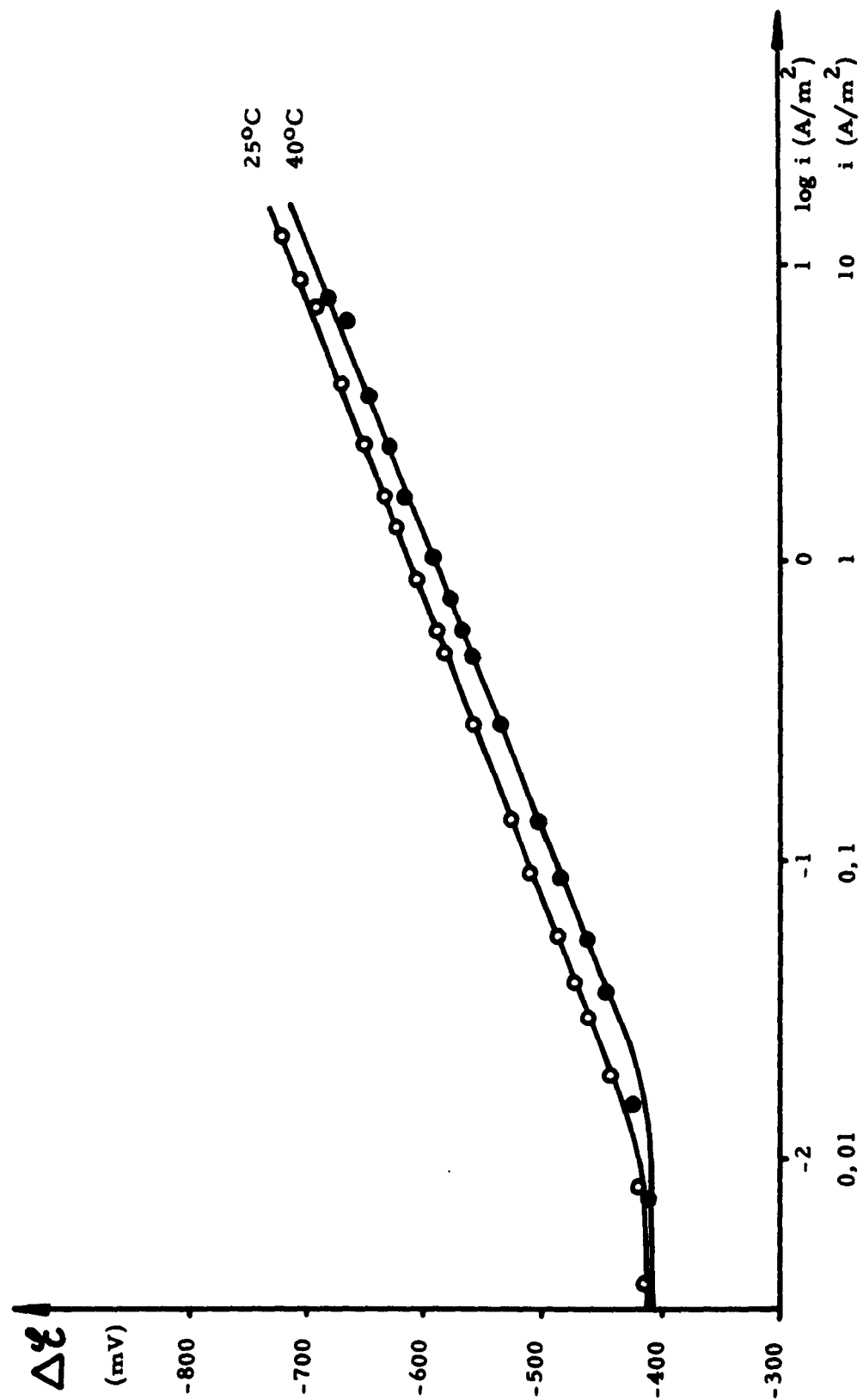
Electrode: (11 $\bar{2}$ 0) Cd

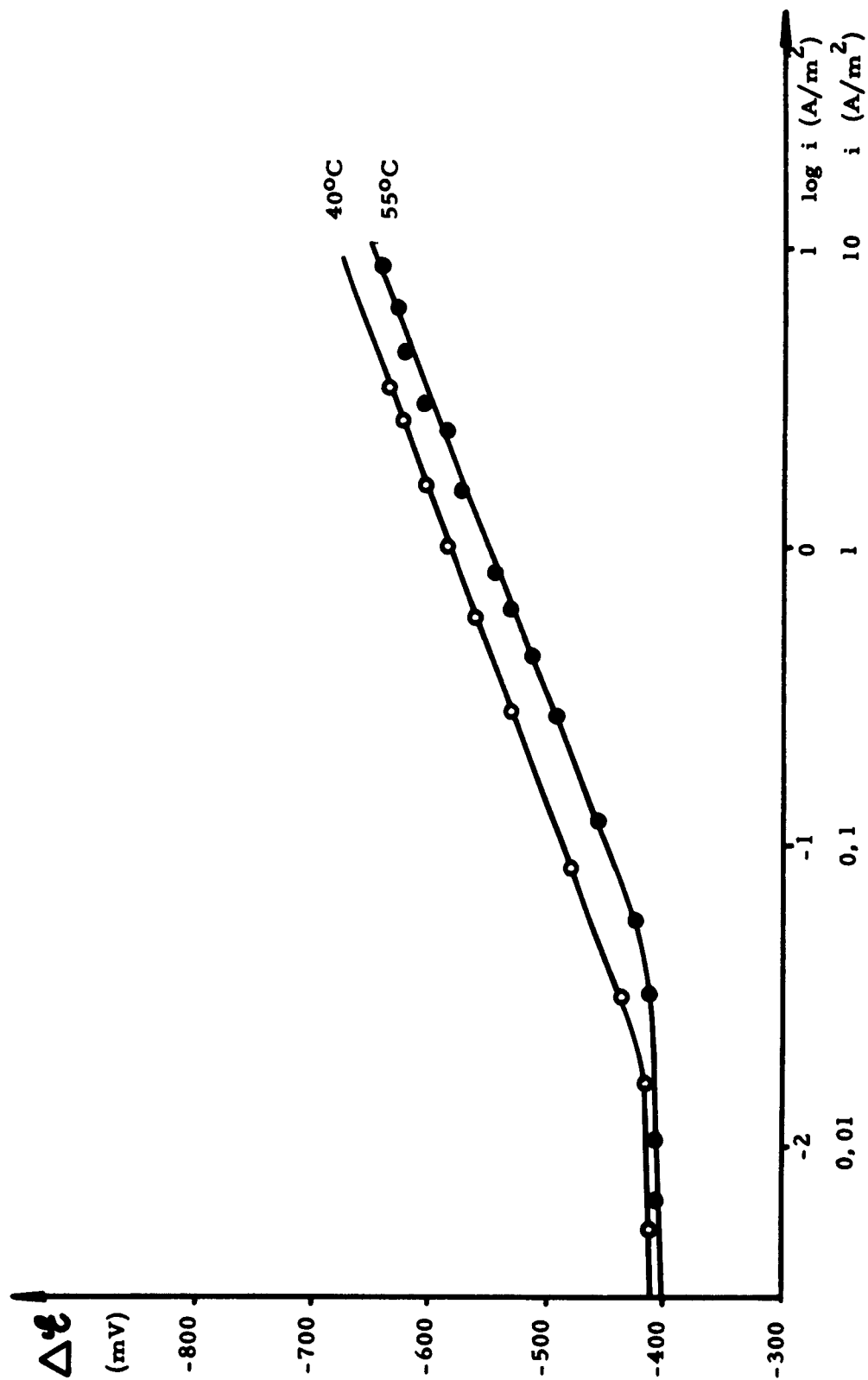
Solution	Temp. (°C)	a (mV)	b (mV)	log i_o (A/m ²)	Overvoltage at		ΔH (Kcal)
					0.1A/m ² (mV)	10A/m ² (mV)	
HClO ₄ 0,005 M	40	585	100	-5,85	485	685	6
	55	550	100	-5,50	450	650	
HClO ₄ 0,035 M	25	510	110	-4,65	425	615	-
	40	500	110	-4,55	430	605	
	55	460	85	-5,40	405	545	

T A B L E V

Electrode: Polycrystalline Cd

Solution	Temp. (°C)	a (mV)	b (mV)	log i_o (A/m ²)	Overvoltage at		ΔH (Kcal)
					0.1A/m ² (mV)	10A/m ² (mV)	
HClO ₄ 0,005 M	25	565	145	-4,00	425	705	-
	40	545	130	-4,20	415	675	
	55	510	130	-3,90	375	635	
HClO ₄ 0,020 M	25	635	150	-4,25	480	790	5
	40	610	160	-3,80	435	770	
	55	610	160	-3,85	490	765	

Fig. 1 - (10 $\bar{1}0$)Cd/0.020 M HClO₄

Fig. 2 - (1120) Cd/0.005 M HClO₄

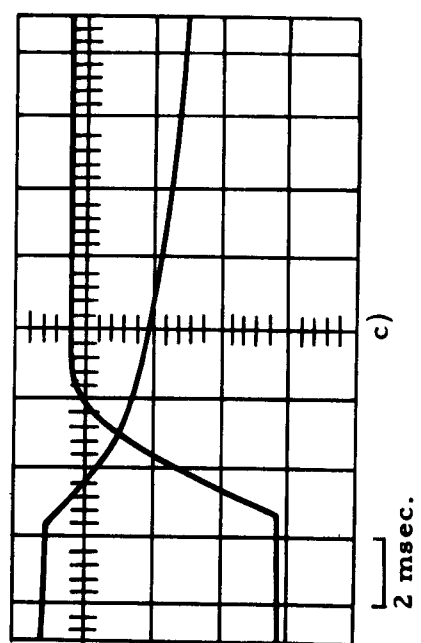
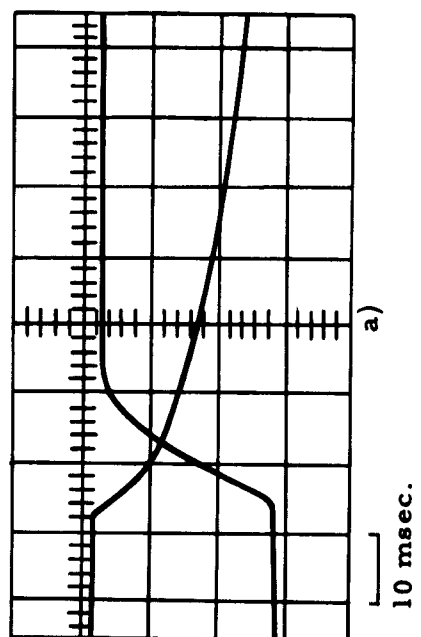
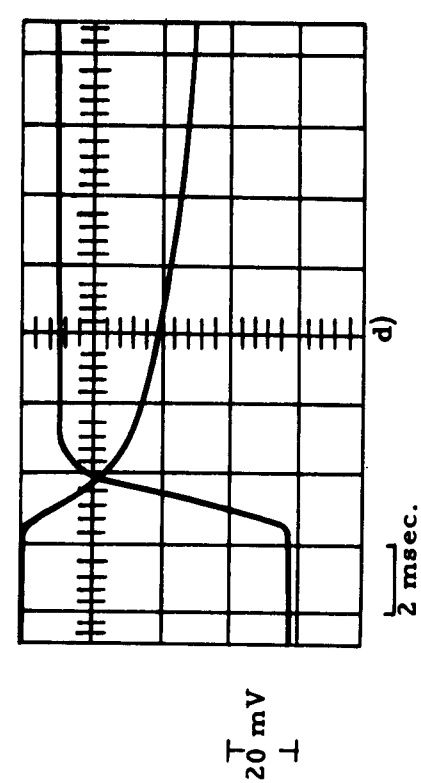
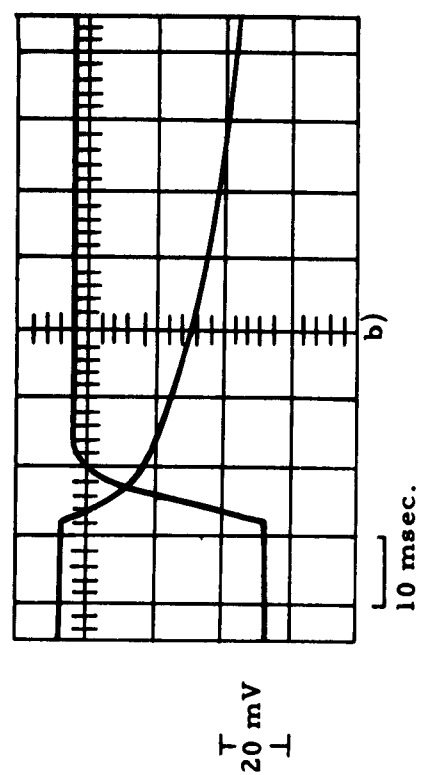


Fig. 3 - Overvoltage versus time oscillograms (0001) Cd/0,035 M HClO_4
a) $i = 3 \text{ A/m}$; b) $i = 5 \text{ A/m}$; c) $i = 10 \text{ A/m}$; d) $i = 30 \text{ A/m}$.

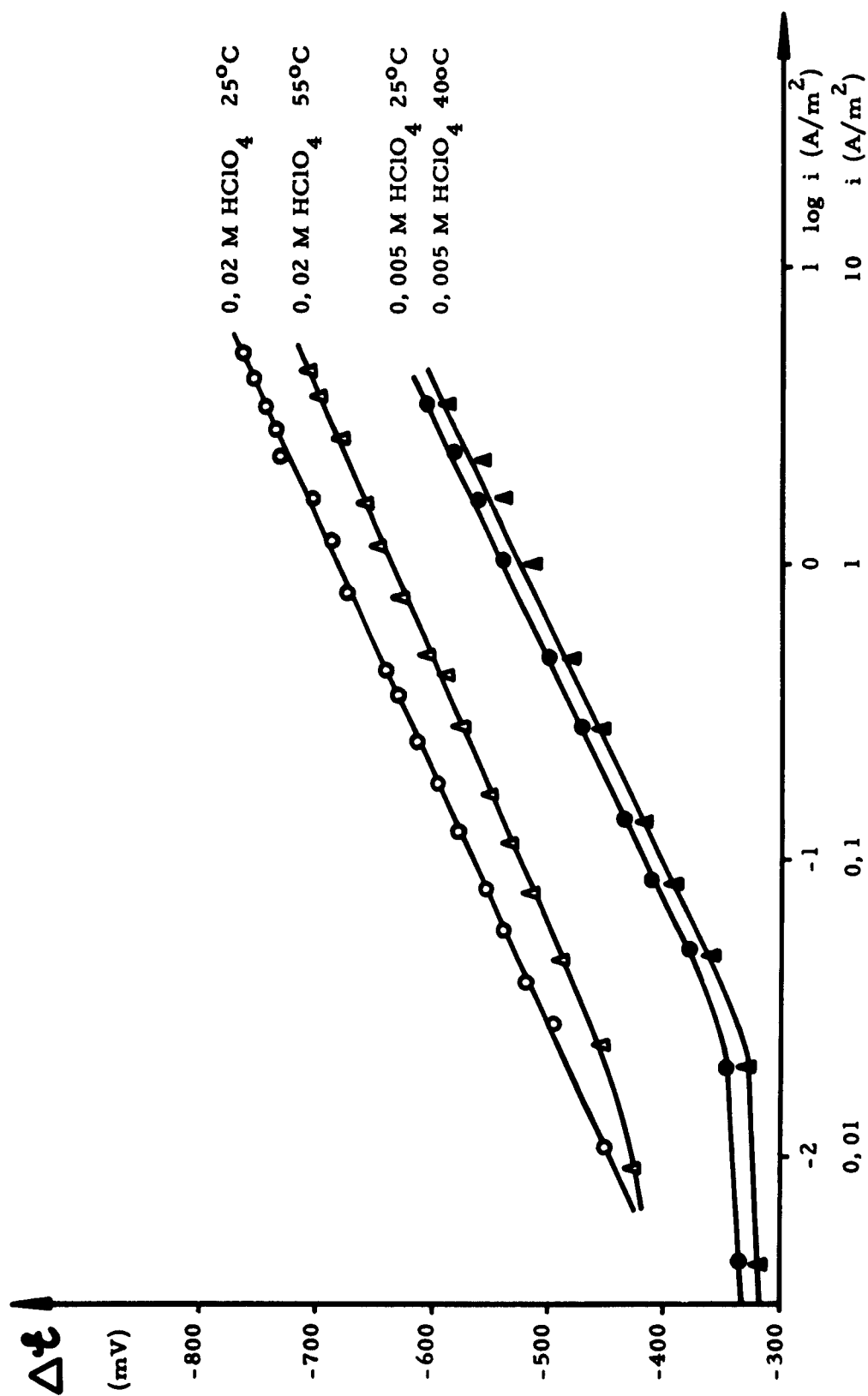


Fig. 4 - (0001) Cd/HClO₄

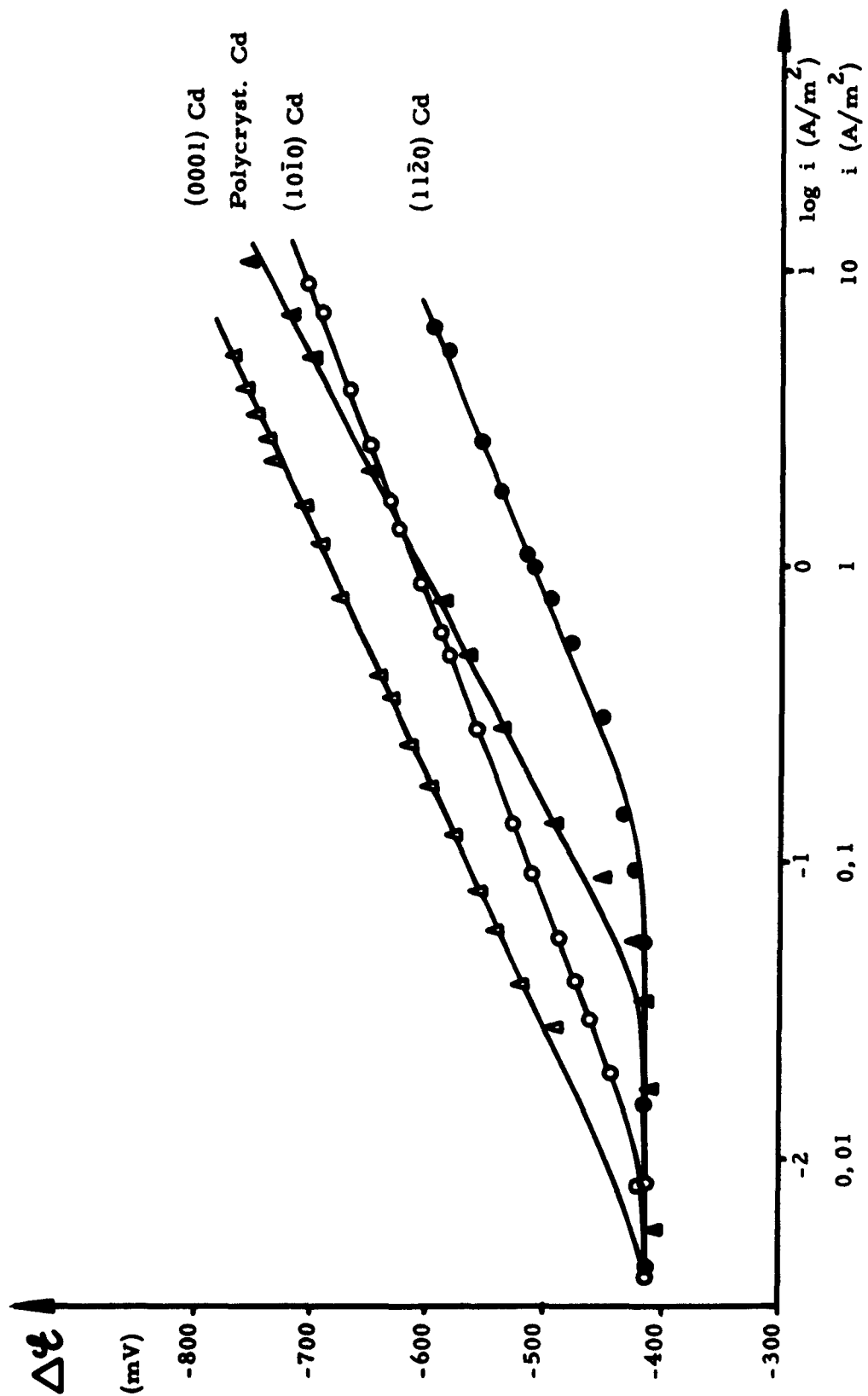


Fig. 5 - Behavior in concentrate perchloric acid. $t = 25^\circ\text{C}$.

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